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Multilayer and functional coatings on carbon nanotubes using atomic layer deposition

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Atomic layer deposition (ALD) can be used to deposit ultra-thin and conformal films on flat substrates, high aspect ratios structures and particles. In this paper, we demonstrate that insulating, multilayered and functionalized ALD coatings can also be deposited conformally on carbon nanotubes. Multilayered coatings consisting of alternating layers of dielectric and conductive materials, such as Al_2O_3 and W, respectively, are deposited on conductive multi-walled carbon nanotubes. This coated carbon nanotube can function as a nanoscale coaxial cable. Thin layers of Al_2O_3 ALD are also used as a seed layer to functionalize nanotubes. A carbon nanotube was made highly hydrophobic using an Al_2O_3 ALD seed layer followed by the attachment of perfluorinated molecules. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2053358]

Widespread interest exists for using carbon nanotubes to fabricate devices. Nanotubes possess many extraordinary properties such as high strength and large electrical conductivity.[1–5] Carbon nanotubes are desirable for future generations of mechanical and electrical devices with applications ranging from backend interconnects to biological probes. The success of many of these applications depends on the deposition of insulating, passivating, or functional films on the carbon nanotubes.[6,7] In this paper, we demonstrate the deposition of insulating, multilayer, and functional films on carbon nanotubes using atomic layer deposition (ALD) techniques.

ALD is a vapor phase thin film growth technique allowing atomic-scale thickness control.[8,9] The technique is based on a sequence of two self-limiting reactions between gas phase precursor molecules and a solid surface. During the reaction sequence, only one reactant is present in the reaction zone at a time. This procedure prevents unwanted gas phase reactions in contrast to chemical vapor deposition. Because only a finite number of reactive sites exist on the surface, reactions with these surface species are inherently self-limiting. Dense and pinhole-free films are produced when these two reactions are allowed to go to completion. Furthermore, since gas phase reactants are utilized, ALD does not require line-of-sight. Conformal coatings can be applied to very high aspect ratio geometries and porous structures.

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Conformal Al_2O_3 ALD coatings have been previously reported on multi-walled carbon nanotubes.[10] This paper expands on this work and presents three applications of ALD on carbon nanotubes. First, a dielectric layer of Al_2O_3 ALD is coated on carbon nanotubes to isolate and insulate the nanotubes from their surroundings. Second, multiple insulating and conductive ALD films are deposited on a conductive carbon nanotube core to fabricate a nanotube multilayer coaxial cable. This novel coaxial cable could be used as a neuronal probe similar in principal to a patch clamp.[11] Third, a seed layer of Al_2O_3 ALD is grown on carbon nanotubes to provide a high concentration of surface hydroxyl (-OH) groups for the attachment of functional molecules. High-resolution transmission electron microscopy (TEM) images of the ALD coatings are obtained to demonstrate the presence and conformality of these films on the carbon nanotubes.

Multi-walled carbon nanotubes were obtained from commercial sources. After dispersion using toluene and sonication, the nanotubes were placed on holey carbon films on copper grids for subsequent TEM analysis. After initial characterization with TEM, the grids were placed in the ALD reactor and coated with the desired film.[12] No special preparation steps were necessary before coating the nanotubes. Al_2O_3 ALD coatings were deposited by the following two sequential reactions where the asterisks designate the surface species:[13,14]

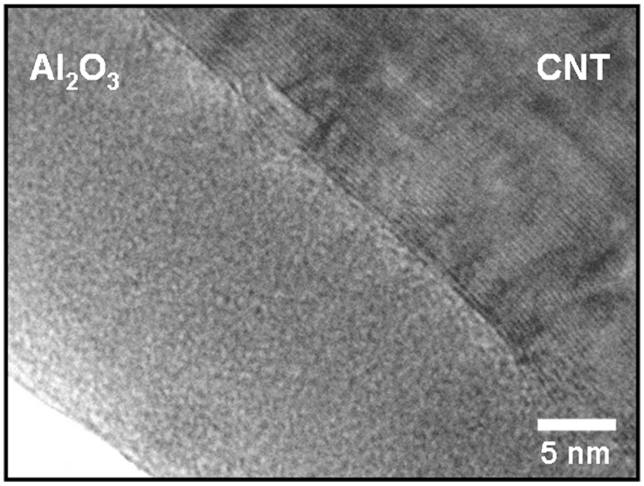

FIG. 1. TEM image of a multi-walled carbon nanotube coated with 25 nm of Al_2O_3 ALD.

$$\text{(A)}\quad AlOH^* + Al(CH_3)_3(g) \rightarrow AlOAl(CH_3)_2{}^* + CH_4(g), \tag{1}$$

$$\text{(B)}\quad AlCH_3{}^* + H_2O(g) \rightarrow AlOH^* + CH_4(g). \tag{2}$$

The carbon nanotubes were first exposed to trimethylaluminum [$Al(CH_3)_3$] and then to the subsequent water exposure. This pattern was repeated to obtain the desired film thickness. At 177 °C, the growth rate for Al_2O_3 ALD was 0.12 nm per AB cycle. Including purging following each reactant exposure, each AB cycle required 12 sec.

A TEM image of a carbon nanotube coated with Al_2O_3 ALD at a deposition temperature of 177 °C is shown in Fig. 1. The Al_2O_3 ALD film thickness is 25 nm. The graphitic structure of the carbon nanotube is clearly visible in this TEM image. A fast Fourier transform (FFT) micrograph of the graphitic structure indicates that the lattice spacing of the graphitic structure is 0.34 nm.

Al_2O_3 ALD films have been found to be excellent insulators.[15] These films display extremely low leakage and have a dielectric constant of approximately 7.5.[15] This Al_2O_3 ALD film on the carbon nanotube should be useful as a dielectric layer to isolate the nanotube from its surroundings.

Multilayered ALD coatings were deposited on carbon nanotubes using successive Al_2O_3 ALD, W ALD, and Al_2O_3 ALD. The Al_2O_3 ALD and W ALD were deposited to obtain individual film thicknesses of ~20 nm. Al_2O_3 was deposited first using the reactions described above and a deposition temperature of 125 °C to form the inner insulating layer. At 125 °C, the growth rate for Al_2O_3 ALD was about 0.13 nm per AB cycle.[16] A typical AB cycle required 44 sec including purging following each reactant exposure. The middle conductive layer was deposited using W ALD.[17] The W ALD surface chemistry required alternating exposures of WF_6 and Si_2H_6. The W ALD film growth was achieved according to the following surface reactions where silicon serves as a sacrificial species:[17,18]

$$\text{(A)}\quad WSiHFSiH_3^* + 2WF_6(g) \rightarrow WWWF_4^* + 2SiF_4 + (3/2)H_2(g) + HF(g), \tag{3}$$

$$\text{(B1)}\quad WF_4^* + Si_2H_6 \rightarrow WSiH_2F^* + SiHF_3(g) + (3/2)H_2, \tag{4}$$

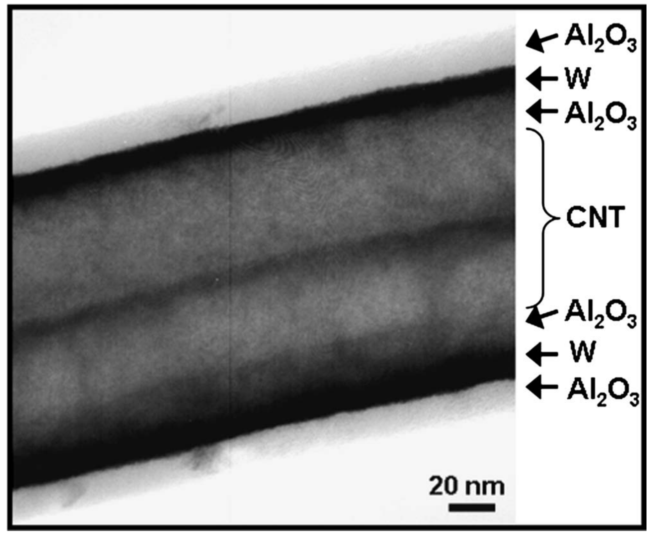

FIG. 2. TEM image of a multi-walled carbon nanotube coated with a multilayered ALD film consisting of an inner Al_2O_3 ALD layer, a middle W ALD layer, and an outer Al_2O_3 ALD layer.

$$\text{(B2)}\quad WSiH_2F^* + (1/2)Si_2H_6 \rightarrow WSiHFSiH_3^* + (1/2)H_2. \tag{5}$$

The growth rate at 125 °C was 0.35 nm per AB cycle and one AB cycle required 61 sec. Following this W ALD layer, a final Al_2O_3 ALD layer was added to insulate the multilayer structure.

The $Al_2O_3/W/Al_2O_3$ coated nanotubes were examined using TEM. The TEM image displayed in Fig. 2 clearly reveals the presence of discrete layers surrounding the carbon nanotube. The high atomic number W layer is highly attenuating and produces a dark region compared with the low atomic number Al_2O_3 layer. The W layer yields the highest contrast and obscures the inner Al_2O_3 ALD layer. This multilayer coated carbon nanotube could be used as a nanotube coaxial cable.

ALD techniques have been previously demonstrated to functionalize various surfaces and render them highly hydrophobic.[19] This technique utilizes an Al_2O_3 ALD seed layer and the subsequent adsorption of a functional hydrophobic monolayer. In this paper, an Al_2O_3 ALD seed layer with a thickness of 25 nm was deposited at 140 °C using the chemistry described above. This Al_2O_3 layer provides a dense and uniform concentration of surface -OH groups on the nanotube.[14] A hydrophobic precursor, tridecafluoro-1,1,2,2-tetrahydro-octyl-methyl-bis(dimethylamino)silane [$C_8F_{13}H_4(CH_3)Si(N(CH_3)_2)_2$], was then chemically bonded to the surface hydroxyl groups on the ALD seed layer. On flat substrates, this procedure produces a film that is highly hydrophobic with a water contact angle of 108°.[19]

Due to poor contrast, the hydrophobic layer was difficult to observe on the Al_2O_3 ALD seed layer with TEM. However, the TEM images suggested that the hydrophobic layer was present with a thickness of approximately 1 nm. This hydrophobic layer thickness agrees well with the expected thickness of ~0.9 nm for the fully extended alkyl chain assuming an all trans configuration with tetrahedral angles. Different molecules could also be reacted with the -OH groups on the Al_2O_3 seed layer to produce a variety of functionalities such as more hydrophilic or biocompatible surface

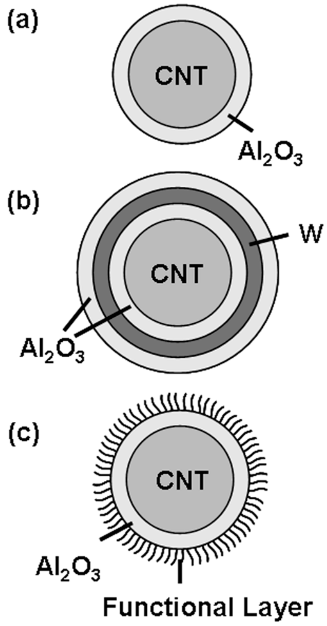

FIG. 3. Schematic cross-sectional drawings of carbon nanotubes coated with (a) Al_2O_3 ALD film, (b) multilayered $Al_2O_3/W/Al_2O_3$ ALD film, and (c) functionalized monolayer on an Al_2O_3 ALD seed layer.

coatings. This surface functionalization allows for easy customization of carbon nanotubes.

In conclusion, ALD techniques were demonstrated for depositing insulating, multilayered, and functionalized coatings on carbon nanotubes as illustrated in Fig. 3. This paper described the deposition of an insulating Al_2O_3 ALD layer [Fig. 3(a)] and the construction of a nanoscale coaxial cable consisting of a carbon nanotube center, an inner insulating Al_2O_3 ALD layer, a middle conductive W ALD layer, and an outer insulating Al_2O_3 ALD layer [Fig. 3(b)]. In addition, a carbon nanotube was functionalized with a hydrophobic coating on an Al_2O_3 ALD seed layer [Fig. 3(c)]. Variations of these techniques can be easily customized to deposit a wide range of coatings to serve multiple purposes. ALD coatings should play a key role in the development of nanotechnology based on carbon nanotubes.

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